

L22 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 1998:25567 CAPLUS
 DN 128:91574
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 TI Galvanized steel sheets having mercaptide coatings for good lubrication and stain prevention
 IN Matsusaki, Akira; Kato, Hiroyuki; Sagiya, Masaru
 PA Nippon Kokan Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 3 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C23C022-53
 ICS C23F011-00; C23F011-16
 CC 55-6 (Ferrous Metals and Alloys)
 FAN.CNT 1

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PI	JP 10001784	A	19980106	JP 1996-173048	19960612 <--
PRAI	JP 1996-173048		19960612		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 10001784	ICM	C23C022-53
	ICS	C23F011-00; C23F011-16
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	IPCR	C23C0022-05 [I,C*]; C23C0022-53 [I,A]; C23F0011-00 [I,C*]; C23F0011-00 [I,A]; C23F0011-10 [I,C*]; C23F0011-16 [I,A]

AB The title sheets comprise galvanized steel sheets with coatings containing mercaptide compds. from reaction products of thiol compds. and a part of Zn-based platings and optionally thiol compds. The sheets have good press formability without coating oils.

ST mercaptide coating galvanized steel lubrication; thiol coating galvanized steel

IT Coating materials
 (galvanized steel sheets having coatings containing mercaptide (and thiols) for lubrication and stain prevention)

IT Galvanized steel
 RL: TEM (Technical or engineered material use); USES (Uses)
 (galvanized steel sheets having coatings containing mercaptide (and thiols) for lubrication and stain prevention)

IT 109-79-5, 1-Butanethiol 112-55-0, 1-Dodecanethiol 638-16-4, 1,3,5-Triazine-2,4,6-trithiol 2885-00-9, 1-Octadecanethiol
 RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)
 (galvanized steel sheets having coatings containing mercaptide (and thiols) for lubrication and stain prevention)

RN 109-79-5
 RN 112-55-0
 RN 638-16-4
 RN 2885-00-9

L22 ANSWER 2 OF 3 WPIX COPYRIGHT 2007 THE THOMSON CORP on STN
 AN 1998-115039 [11] WPIX
 DNC C1998-038216 [11]
 TI Superior zinc group plating steel plate having lubricity and resistance to contamination - uses skin layer with mercaptide compound which is reaction product of thiol compound and part of zinc group plating skin layer
 DC M14

IN KATO H; MATSUZAKI A; SAGIYAMA M
 PA (NIKN-C) NKK CORP
 CYC 1
 PI JP 10001784 A 19980106 (199811)* JA 3[0] <--
 ADT JP 10001784 A JP 1996-173048 19960612
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 IPCR C23C0022-05 [I,C]; C23C0022-53 [I,A]; C23F0011-00 [I,A]; C23F0011-00
 [I,C]; C23F0011-10 [I,C]; C23F0011-16 [I,A]
 AB JP 10001784 A UPAB: 20050520
 The plate has a surface formed with a skin layer containing a mercaptide
 compound which is a reaction product of a thiol compound and a part of
 zinc group plating skin layer. The skin layer is preferably formed with a
 partial zinc group plating layer and a reaction product of alkyl thiol
 compound containing a thiol group mercaptide compound with 8 or more
 number of carbons branched to the lens of an alkyl group.
 USE - In galvanised iron sheets for press stamping.
 ADVANTAGE - Demonstrates high level lubricity more than lubrication
 capacity of rapid drying oil currently used. Demonstrates high level
 resistance to contamination. Prevents adhesion of stain during storage and
 transportation pertinently.
 MC CPI: M14-D; M14-F

 L22 ANSWER 3 OF 3 JAPIO (C) 2007 JPO on STN
 AN 1998-001784 JAPIO
 TI GALVANIZED STEEL SHEET EXCELLENT IN LUBRICITY AND STAIN RESISTANCE
 IN MATSUZAKI AKIRA; KATO HIROYUKI; SAGIYAMA MASARU
 PA NKK CORP
 PI JP 10001784 A 19980106 Heisei
 AI JP 1996-173048 (JP08173048 Heisei) 19960612
 PRAI JP 1996-173048 19960612
 SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1998
 IC ICM C23C022-53
 ICS C23F011-00; C23F011-16
 AB PROBLEM TO BE SOLVED: To produce a galvanized steel sheet having excellent
 lubricity so as to withstand oilless press forming and furthermore
 excellent in stain resistance.
 SOLUTION: This galvanized steel sheet is the one in which the surface of a
 galvanized steel sheet is applied with coating composed of a mercaptide
 compound which is the reaction product between a thiol compound and a part
 of galvanizing coating film or with coating film composed of a thiol
 compound and a mercaptide compound which is the reaction product between a
 thiol compound and a part of galvanizing coating film. In this case, it is
 preferably that the mercaptide compound is the reaction product between an
 alkylthiol compound in which the terminal or both terminals of
 straight-chain ≥ 8 C alkyl groups have thiol groups and a part of
 galvanizing coating film.
 COPYRIGHT: (C)1998,JPO

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PTO 07-3931

CC=JP DATE=19980106 KIND=A
PN=10001784

GALVANIZED STEEL SHEET EXCELLENT IN
LUBRICITY AND STAIN RESISTANCE
[Junkassei To Taiosensei Ni
Yugureta Aenkei Nukki Kohan]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C.

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APPLICANT	(71):	NIPPON KOKAN KOJI CORP.
TITLE	(54):	GALVANIZED STEEL SHEET EXCELLENT IN LUBRICITY AND STAIN RESISTANCE
FOREIGN TITLE	[54A]:	JUNKASSEI TO TAIIOSENSEI NI YUGURETA AENKEI NUKKI KOHAN

(54) [Title of the Invention]

/1*

Galvanized Steel Sheet Excellent in Lubricity and Stain Resistance

[Claim(s)]

/2

[Claim 1] A galvanized steel sheet excellent in lubricity and stain resistance characterized by having a coating comprising a mercaptide compound, which is a reaction product between a thiol compound and a portion of a galvanizing coating, or having a coating comprising a thiol compound and a mercaptide compound, which is a reaction product between a thiol compound and a portion of a galvanizing coating.

[Claim 2] The galvanized steel sheet having excellent lubricity and stain resistance of Claim 1 characterized by the mercaptide compound being a reaction product between an alkyl thiol compound having thiol group(s) at one or both terminals of a straight chain alkyl group having eight or more carbons and a portion of a galvanizing coating.

[Detailed Specifications]

[0001] [Technical Field of the Invention]

This invention relates to a surface galvanized steel sheet having excellent lubricity and stain resistance.

[0002] [Prior Art]

Galvanized steel sheets, such as zinc-based plated steel sheets, alloyed melt-galvanized steel sheets and Al-Zn-based plated steel sheets, have been used widely in the pastas blanks for stamping. To improve the workability of these zinc-plated steel sheets during stamping, a press oil generally is applied onto the surface of the plated steel sheet.

* Number in the margin indicates pagination in the foreign text.

However, recently, galvanized steel sheets for which the degreasing step can be omitted from the viewpoint of environmental conservation, and in short, which can be without being degreased after stamping are in strong demand. Thus, quick-drying oils that are applied press oils which dry spontaneously after stamping are used in general, but recently, a much higher level of press moldability has been demanded for stamping, and it has become a difficult situation to sufficiently meet such a demand using a conventional quick-drying oil.

[0003] In addition, rain water adheres to a galvanized steel sheet during the storage and transport thereof in the period after its manufacture up until it is machined by the user, and contaminants, such as C, Ca and Si, which are contained in rain water, remain and adhere to the surface of the plated steel sheet after the rain water has dried, so there is a problem because this compromises the appearance of the plated steel sheet. A method in which the surface on which oiling is performed on the surface of the steel sheet is hydrophobicized is generally used as a measure against this, but even if the above process is used, dust, dirt, and the like wind up in the oil; hence, staining cannot be prevented enough.

[0004] [Problems to be Solved by the Invention]

Consequently, an object of the present invention is to provide a galvanized steel sheet having excellent lubricity and also outstanding in stain resistance and which can withstand a press-forming without oiling.

[0005] [Means for Solving the Problems]

To achieve such an object, the characteristic constitutions of the present invention are as follows.

(1) A galvanized steel sheet excellent in lubricity and stain resistance characterized by having a coating comprising a mercaptide compound, which is a reaction product between a thiol compound and a portion of a galvanizing coating, or having a coating comprising a thiol compound and a mercaptide compound, which is a reaction product between a thiol compound and a portion of a galvanizing coating.

(2) The galvanized steel sheet in (1) above; said galvanized steel sheet having excellent lubricity and stain resistance characterized by the mercaptide compound being a reaction product between an alkyl thiol compound having thiol group(s) at one or both terminals of a straight chain alkyl group having eight or more carbons and a portion of a galvanizing coating.

[0006] [Embodiments of the Invention]

A characteristic feature of the present invention is to provide a coating comprising a mercaptide compound, which is a reaction product between a thiol compound and a portion of the galvanizing coating (including cases in which unreacted thiol compound remains), on the surface of a galvanized steel sheet. When the thiol compound is applied onto the galvanized steel sheet, a mercaptide compound having a film thickness on the order of several molecules is formed by reacting with the zinc or zinc oxide on the surface of the plated coating to a state in which the plated surface is covered by the mercaptide compound. An inventor of the present invention discovered that extremely excellent lubricity and stain resistance could be obtained by forming a coating of such a mercaptide compound on the surface of a galvanized steel sheet.

[0007] Melt-galvanized steel sheets, electro-galvanized steel sheets, alloyed melt-galvanized steel sheet, Zn-Al-based alloy-plated steel sheets, Al-Zn-based alloy-plated steel plates, and the like can be cited for the target galvanized steel sheet of the present invention. Since the content of the mercaptide compound in the coating (amount of thiol adsorbed in the surface of the galvanized steel sheet) is a tiny amount, it is difficult to quantitatively limit it. However, by using an analysis means, such as an X-ray electron analyzer (XPS), the presence of the adsorbed thiol compound can be confirmed by examining the state of the C, S, O and Zn. As long as it is contained to the extent that the thiol adsorption can be confirmed by such a means, the desired lubricity and stain resistance are obtained. Moreover, it is not a problem if unreacted thiol compound is present in the coating according to the present invention. As long as the mercaptide compound is produced, the desired lubricity is obtained even if unreacted thiol compound is present.

[0008] A general method for forming the above-mentioned coating includes a method in which a thiol compound dissolved or diluted with ether, alcohol, water, or the like is applied onto a plated steel sheet, and thus, enough lubricity and stain resistance area obtained, but after this, a sealing treatment is further carried out on the coating defects at the molecular level by dipping it in hexane or the like, and extremely excellent lubricity and stain resistance are obtained. In addition, although the type, chemical structure, and the like of the thiol compound used to form the mercaptide compound are not limited, an alkyl thiol compound having thiol group(s) at one or both ends of a straight chain alkyl group

having eight or more carbons may be cited as an especially ideal thiol compound. Of these, alkyl thiols, such as 1-octadecane thiol, /3
1-hexadecane thiol, 1-dodecane thiol and 1-octathiol, may be cited as examples of the alkyl thiol having a thiol group at one end of the alkyl group. Moreover, n-decane thiol ($C_{10}H_{20}(SH)_2$) may be cited for the alkyl thiol having thiol groups at both ends of an alkyl group. These thiol compounds have an effect for improvement with an especially excellent lubricity.

[0009] Moreover, it is not preferable if the acidity of the thiol compound increases excessively because the etching action on the surface of the plated steel sheet increases. The acidity of the thiol compound generally is affected by the size of the alkyl group. The larger the alkyl group, the smaller the acidity is. In addition, since there is a tendency for the acidity of the thiol compound to decrease in order of a primary, secondary and tertiary thiol compound, this is a useful criterion for selecting the thiol structure. Therefore, it is preferable to select the structure of the thiol compound, depending on the blank.

[0010] [Practical Examples]

The materials offered for testing wherein electro-galvanized steel sheet were used as the plated steel sheet blanks, were prepared, as follows, and the lubricity (coefficient of thermal expansion), stain resistance and water repellency (contact angle to water) of these materials offered for testing were measured and evaluated. The results thereof are shown in Table 1.

Practical Example 1 (Example of present invention)

A galvanized steel sheet was dipped in a solution in which 5 millimoles of 1-octadecane thiol were added to a mixed solvent (4:1) of ethanol and water, and dried.

Practical Example 2 (Example of present invention)

A galvanized steel sheet was dipped in the same thiol-containing solution as in Practical Example 1, subsequently dipped in hexane, and dried.

[0011] Practical Example 3 (Example of present invention)

A galvanized steel sheet was dipped in a solution in which 5 millimoles of 1-butane thiol were added to a mixed solvent (4:1) of ethanol and water, and dried.

Practical Example 4 (Example of present invention)

A galvanized steel sheet was dipped in a solution in which 5 millimoles of 1-dodecane thiol were added to butyl cellosolve, and dried.

Practical Example 5 (Example of present invention)

A galvanized steel sheet was dipped in an aqueous solution to which 5 millimoles of 1,3,5-triazine-2,4,6-trithiol were added, and dried.

Practical Example 6 (Comparative Example)

A galvanized steel sheet used as is

Practical Example 7 (Comparative Example)

A commercially-available quick-drying oil "G6211" (manufactured by Kohsakuyu Co., Ltd.) was applied onto a galvanized steel sheet.

[0012] Lubricity: The lubricity was evaluated by inserting the measurement sample in a jig manufactured from SKD11, and measuring the

tensile load P while performing a planar drawing test at a pressing load W of 0.8 kgf/mm^2 (drawing speed: 200 mm/min.) by basing this on the coefficient of thermal expansion ($=P/(W \times 2)$). The stain resistance was evaluated from the ΔE of the sample obtained by applying a solution in which water was mixed at a weight ratio of 1:1 by using twelve kinds of carbon black used for a test stipulated by JIS Z-8901, set aside for 24 hours, and cleaned by washing with water. Moreover, when ΔE ($=$ geometric mean of $(L, a, b$ values after test) $- (L, a, b$ values before test) is $\Delta E \leq 1$, it is a level at which staining cannot be confirmed visually. The water repellency was evaluated by finding the contact angle to water using pure water in a droplet test.

[0013] According to Table 1, the lubricity and stain resistance of the Practical Examples 1 to 5, which are the present practical examples, are improved more greatly than those of the untreated comparative example (Practical Example 6) and the comparative example in which a quick-drying oil was applied (Practical Example 7). In addition, Practical Examples 1 to 4 are examples in which a specific alkyl thiol compound stipulated in claim 2 was used. A far superior lubricity than that in Practical Example 5 is obtained.

[0014] [Table 1]

TABLE 1

No.	供 試 材	潤 滑 性 (摩擦係数)	耐汚染性 ΔE	撥 水 性 対水接触角 (°)	区 分
1	1-オクタデカンチオール含有溶液浸漬→乾燥	0.07	0.5	120	本発明例
2	1-オクタデカンチオール含有溶液浸漬→ヘキサン浸漬→乾燥	0.07	0.2	130	本発明例
3	1-ブタンチオール含有溶液浸漬→乾燥	0.09	0.7	100	本発明例
4	1-ドデカンチオール含有溶液浸漬→乾燥	0.09	0.7	120	本発明例
5	1,3,5-トリアジン-2,4,6-トリチオール含有溶液浸漬→乾燥	0.12	0.8	110	本発明例
6	無処理	0.45	3.8	70	比較例
7	速乾油塗布	0.15	1.0	110	比較例

Key:

No.	Sample Offered for Testing	Lubricity (Coefficient of Thermal Expansion)	Stain Resistance ΔE	Water Repellency (Contact Angle to Water (°))	Category
1	Dip in 1-octadecane thiol-containing solution and dry				Example of present invention
2	Dip in 1-octadecane thiol-containing solution then in hexane and dry				Example of present invention
3	Dip in 1-butane thiol-containing solution and dry				Example of present invention
4	Dip in 1-dodecane thiol-containing solution and dry				Example of present invention
5	Dip in 1,3,5-triazine-2,4,6-tri thiol-containing solution and dry				Example of present invention
6	Untreated				Comparative example
7	Apply quick-drying oil				Comparative example

[0015] [Advantages of the Invention]

Staining can be prevented suitably during storage and transport because the galvanized steel sheet of the present invention, which was described above, has a higher level of lubricity than the lubricating performance of a quick-drying oil used in the past, and moreover, it has a higher level of stain resistance.